Indian J. Phys. **77B** (5), 525-528 (2003)

AN INTERNATIONAL JOURNAL
IJP

Ultrasonic studies on solutions of hydroxy propyl methyl cellulose phthalate in alcohols and acetone mixture

D Geetha and C Rakkappan*

Department of Physics, Annamalai University, Annamalai Nagar-608 002, Tamil Nadu, India

E-mail : rakk_c@rediffmail.com

Received 5 November 2001, accepted 19 June 2003

Abstract Ultrasonic velocity, density and shear viscosity have been measured for solutions of hydroxy propyl methyl cellulose phthalate (HPMCP) in methanol, ethanol, propanol and n-butyl alcohols with Acetone mixture (1:1). The ultrasonic velocity and absorption data are presented at 303 K. By taking measurements at several concentrations of each solution, information about the molecular interaction between the solute and solvent molecules was obtained.

Keywords Ultrasonic studies, polymer solutions, solute-solvent interaction

PACS Nos. 43.35.Bf, 31.70.Dk

1. Introduction

Polymeric articles are often moulded through solutions or gels and the structure of the later determines to a considerable extent the structure of the polymeric article being moulded (fibres, films, lacquer coats *etc*). Therefore, the study of structure of the solution is no less important than the study of the structure of polymer itself.

The structure of polymer solutions were studied from the same standpoint as structure of the liquids and liquid solutions of low molecular substance. The phenomena of a preferential interaction between unlike molecules (solvation) or similar ones (association) is observed, depending on the degree of affinity between the components. Thus, solvates and associates are elements of the structure of a solution. When the polymer dissolves, the structure of both the components may change and the phenomena of solvation and association are observed depending on the nature of the solvent (*i.e.* good or poor solvent).

A review of literature [1-6] on acoustical studies of polymer solutions reveals that ultrasonic velocity and absorption measurements are used to understand the nature of molecular interactions in these systems. Hydroxy propyl methyl cellulose phthalate has a variety of applications in medical field in the preparation of ophthalmic solutions and it contains an antimicrobial preservative. Acetone and alcohols are very good solvents for this polymer. Hence, ultrasonic studies were done at 303K in the HPMCP dissolved in alcohols : acetone (1:1) mixture at 303 K.

* Corresponding Author

2. Experimental

HPMCP (molecular weight 20,000) was obtained from Fluka Company. The alcohols and acetone were obtained from BDH Company. They were used after standard purification [7,8].

The ternary solutions were prepared by adding a known weight of polymer (HPMCP) to a fixed volume of solvents *viz.*, acetone and alcohols (1:1) and then stirring under reflux using a magnetic stirrer until a clear solution was obtained. Due to its high viscous nature, the low concentration range of the polymer were studied *i.e.*, 0 % to 2.5 % (weight %). 0.0% corresponds to alcohol and acetone (1:1) mixture. The ultrasonic velocity and absorption were measured using a pulse echo interferometer (10 MHz) by the standard procedure [9]. Accuracies in the measurement of velocity and absorption are 0.01 % and 1 % respectively. Densities were determined using a specific gravity

bottle and viscosity was estimated using a Ostwald Viscometer. All the measurements were carried out at 303 K.

3. Physical parameters

The various physical parameters were calculated from the measured values of density (ρ), viscosity (η), ultrasonic velocity (C) and absorption $(\alpha / f^2)_{obs}$ using the standard formula.

i) Adiabatic compressibility $\beta_s = 1/C^2\rho$.

ii) Internal pressure

$$P_i v = TV/\beta_s,$$

where v is the ratio of specific heat capacities and V is the thermal expansion.

iii) Intermolecular free length $L_f = K\beta_s^{1/2}$. The values of K for different temperature were taken from the work of Jacobson [10].

iv) Classical absorption : $(\alpha / f^2)_{obs} = 8\pi^2\eta_s / 3\rho C^3$.

v) Excess absorption :

$$(\alpha / f^2)_{excess} = (\alpha / f^2)_{obs} - (\alpha / f^2)_{class}.$$

4. Results and discussion

It can be seen from the tables (Table 1 and 2), the ultrasonic velocity increases nonlinearly with increase of concentration of polymer in methanol, ethanol with acetone mixtures. In solution of propanol and butanol, ultrasonic velocity remains almost constant throughout the concentration range studied. Adiabatic

Table 1. Ultrasonic velocity and related parameters for the solutions of hydroxy propyl methyl cellulose phthalate in alcohols and acetone (1:1) at 303 K

Concentration weight %	C ms^{-1}	ρ Kgm^{-3}	$\eta \times 10^{-3}$ Nsm^{-2}	$\beta \times 10^{-10}$ N^{-1} m^2	Lf A^0	$P_i v$ pascal	S × 10	R × 10^{-4}	Za Kgm^{-2} s^{-2}
Methanol acetone (1:1)									
0 0	1130 2	787 5	0.4438	9 9412	0.6293	7255	-	5 4512	8 9003
0 5	1134 7	789 5	0 5923	9.8375	0 6260	8382	2 0756	5 445	8 9584
1 0	1136 2	792 3	0 7545	9 7768	0 6216	9475	3 2905	5 4283	9 0021
1 5	1139 6	795 9	0 8013	9 6746	0 6208	9776	5 3361	5 4085	9 0700
2 0	1141 7	797 7	0 9564	9 6173	0 6189	10691	6 4836	5 3996	9 1073
2 5	1148 1	799 8	1 0055	9 4854	0 6147	10951	9 1239	5 3943	9 1825
Ethanol acetone (1 1)									
0 0	1150 7	789 9	0 4635	9 5128	0 6156	5707	-	6 8131	9.1354
0.5	1151 8	791 4	0 6103	9 4648	0.6140	6553	1.0040	6 8009	9 1729
1 0	1152 2	793 5	0 7845	9 4334	0 6130	7445	1 6609	6 7843	9 2003
1 5	1153 3	796 7	0 8678	9 3895	0 6116	7844	2 5793	6 7600	9.2344
2 0	1154 5	798 3	0 9861	9 3646	0.6108	8369	3.1001	6 7486	9 2502
2.5	1155 2	801 5	1 0132	9 3260	0.6095	8503	3 9073	6 7218	9 2820
Propanol acetone (1 1)									
0 0	1157 6	793 9	0 5226	9.4068	0.6121	5151	-	7.8109	9 1901
0 5	1158 4	796.4	0.7345	9.3573	0.6105	6121	1.0470	7 7779	9 2254
1 0	1157.8	798 5	0 8723	9 3423	0 6100	6680	1.3643	7.7768	9 2450
1.5	1158 5	800.7	0 9632	9.3054	0 6080	7.27	2 1448	7 7482	9.2761
2 0	1157 6	801 3	1 0005	9.3129	0 6091	7172	1 9862	7 7404	9 2758
2.5	1156.4	803 5	1.1547	9 3067	0.6089	7719	2.1154	7.7166	9.2916
Butanol acetone (1 1)									
0 0	1185 2	798 6	0 5698	8 9143	0 5959	4700	-	8 7174	9.4650
0 5	1186 2	799 8	0.7015	8.8854	0.5949	5218	0 6451	8.7068	9 4872
1 0	1187.8	800.4	0 8624	8.8553	0.5939	5785	0.8065	8.7042	9.5071
1 5	1188.1	801.6	1 0036	8.8376	0.5933	6246	1.7122	8.6919	9.5238
2 0	1187.1	802 9	1.1563	8 8382	0 5933	6714	1 6988	8.6754	9.5312
2.5	1188.5	804.0	1.3595	8 8053	0 5922	7280	2 4332	8.6666	9.5555

Table 2. Ultrasonic absorption and related parameters for the solutions of hydroxy propyl methyl cellulose phthalate in alcohols and acetone (1:1) at 303 K

Concentration weight %	$(\alpha/f^2)_{obs} \times 10^{-15}$ Npm^{-1} s^2	$(\alpha/f^2)_{class} \times 10^{-15}$ Npm^{-1} s^2	$(\alpha/f^2)_{excess} \times 10^{15}$ Npm^{-1} s^2	$\eta_v \times 10^3$ Ns m^{-2}	$\tau \times 10^{-12}$ sec
Methanol · acetone (1.1)					
0.5	39 90	13.501	26 40	1 5443	2 3203
1.0	40 42	17 069	23.35	1.3769	2 3688
1 5	46.36	17 914	28.45	1 6967	2 7488
2.0	49 13	21 221	27 99	1 6971	2 8810
2.5	50.33	21 841	28 49	1 7487	3 0712
Ethanol · acetone (1 1)					
0.5	40 82	13 2691	27 56	1 6912	2 3828
1 0	44 12	16 997	27.13	1 6695	2 6074
1 5	46 18	18.669	27 52	1 7064	2 7251
2 0	49.45	21.111	28 34	1 7651	2.9298
2.5	56.27	21 559	34 72	2 1765	3.3555
Propanol : acetone (1:1)					
0 5	52 73	15.599	37 131	2.3315	3.1144
1.0	56 23	18 506	37 730	2.3712	3 3245
1.5	59 78	20.341	39 439	2 4900	3 5503
2 0	54 91	21 152	33 758	2 1279	3 2565
2.5	54 32	24 433	29 88	1 8833	3 2195
Butanol acetone (1 1)					
0 5	61 20	13 816	47 39	3 2096	3 6949
1 0	63.20	19 642	43 55	2 5493	3.2975
1 5	71.20	19 627	51 58	3.5178	4 3287
2 0	60 54	22 634	37 91	2 5827	3.6766
2 5	63 80	26 482	37 32	2.5547	3 8932

compressibility is found to decrease nonlinearly with increase of concentration in methanol, ethanol system but the variation in propanol and butanol is linear. The intermolecular free length decreases rapidly in case of methanol and ethanol with acetone mixture. But the decrease is very less in the systems of propanol and butanol mixture. Internal pressure increases with increase of concentration in all the systems. Rao's constants vary nonlinearly with concentration in the lower alcohol systems. The number of solvated molecules per repeat unit is approximately 9 for methanol, 4 for ethanol and 2 for propanol and butanol with acetone mixture.

The increase in ultrasonic velocity with solute concentration in methanol and ethanol with acetone, is due to interaction between solute and solvent molecules. In lower aliphatic alcohol systems, the interaction is more between the high polymer molecules and solvent molecules. At low concentrations, the number of hydrogen bonds formed may be less and at higher concentrations, it may be more due to polymer-polymer interaction. In the present system, the hydrogen bond is formed between the hydrogen of methyl group in HPMCP and the oxygen of hydroxyl group in alcohol [11]. But in the case of higher aliphatic alcohols, the number of sites available for hydrogen bond formation is quite less and the interaction is not much effective, as the number of solvated molecules are less in number. This may be the reason for the constancy of velocity in higher alcohol systems. The rapid decrease of adiabatic compressibility with increase of concentration in methanol and ethanol with acetone system, clearly indicates the formation of a more number of tightly bound systems. Since the velocity increases with concentration and the density does so, the compressibility must decrease with concentration. This could be caused by more rigid liquid structure associated with hydrogen bonding of HPMCP with methanol and ethanol. Such reduction in compressibilities have been found in solutions of cellulose derivatives which is attributed to change in compressibilities of the solvent molecules concerned in solutions [12]. In propanol and butanol with acetone mixture, there is a slight decrease in compressibility with concentration. This implies the increase of density with concentration, which leads to decrease in compressibility. At lower concentration in methanol and ethanol with acetone mixture, the molecules are not closer and thus the intermolecular free length will be high. As the concentration increases, the molecules come closer

through segment-segment interaction and thereby decreasing the intermolecular free length and hence internal pressure increases [13]. Acoustic impedence increases with increasing concentration in lower alcohol which is indicative of strong solvent-polymer interaction and is further supported by increase of Rao's constant and internal pressure [14].

It is observed that $(\alpha / f^2)_{obs}$ values increases with concentration in lower aliphatic alcohol systems, but it remains constant in higher aliphatic alcohol systems. The significant amount of excess absorption indicating dynamic shear viscosity, is not the only relaxation contributing to the relaxation absorption. The other source of relaxation mechanism involved in this systems are the polymer-solvent interaction due to hydrogen bonding and polymer-polymer interaction. In the lower aliphatic alcohol systems, the major role is played by hydrogen bonding, since the observed absorption increases with concentration [15]. The excess sound absorption in the case of higher aliphatic alcohol systems is mainly due to transition from isolated macro molecules to associates and *vice versa* [16], which may be explained as follows. The molecules of cellulose and its derivatives are randomly coiled in solution and also the chains have no overall tendency to adopt any particular conformation In general, the cellulose and its derivative molecules are linear, consists of sufficient number of chain linkages, which is an essential prerequisite for any chain to be randomly coiled. The conformation of chain results from the interactions of the chain segments with its environment. These interaction involve the segments of the same as well as other chain in addition to the solvent. In a good solvent, each chain segment will prefer to contact with solvent molecules rather than with the segments of its own or those of neighbouring chains, because of this, the chain will be extended [17] In a poor solvent like higher aliphatic alcohols, polymer-polymer and solvent-solvent contacts (associates) are favoured, the polymer chain will have a contracted form, hence the variation in observed absorption with concentration is not significant. The number of solvated molecules S and the increase in relaxation time τ in lower aliphatic alcohol systems confirm the polymer-solvent interaction.

References

[1] S K Hassun *Eur Polym. J* **24** 795 (1988)

[2] S Bagchi, S K Nema and R P Singh *Eur Polym J* **22** 851 (1986)

[3] R A Pethrick and B T Poh *Brit Polym J* **15** 149 (1983)

[4] B Saraf and K Samal *Acoustica* **55** 60 (1984)

[5] C Rakkappan, A Srinivasa Rao and B Krishnan *Proc Indian Acad Sci (Chem Sci.)* **101** 429 (1989)

[6] R P Singh and G V Reddy *Acoustica* **55** 342 (1984)

[7] Othemer Kirk *Encyclopedia of Chemical Technology*, **Vol.18** 3rd edn (New York John Wiley) p 214 (1982)

[8] B S Furniss, A J Hannaford, V Rogers, P W G Smith and A R Tatchell Vogel's *Text Book of Practical Organic Chemistry* 4th edn (London Longman) (1978)

[9] K R Srinivasan, S Krishnan and A Srivarman *Proc. Symp Transducer Technology* (Cochin NPOL) 283 (1975)

[10] B Jacobson *Nature* **173** 772 (1954)

[11] Sonali Saha, B Roy, S K Siddhanta and T P Sinha *Indian J Phys* **74A(4)** 379 (2000)

[12] W R Moore *J Polym Sci* **16** 571 (1967)

[13] C Rakkappan and N Punitha *International Conference and Exhibition on Ultrasonics* (New Delhi) **1** 218 (1999)

[14] A R Shah and P H Parsania *Eur Polym. J* **33** 1245 (1997)

[15] E Henry *Bass J Acoust Soc. Am* 283 (1993)

[16] A Tager *Physical Chemistry of Polymers* (Moscow MIR) (1978)

[17] A J Matheson *Molecular Acoustics* (London John Wiley) (1970)